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Abiotic Interactions of Aqueous Chromium Ions with Iron Oxide Surfaces

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We have carried out molecular-level experimental and modeling studies of the interaction of water and Cr(VI)$_{aq}$ with well-characterized single crystal samples of synthetic and natural hematite and magnetite in order to gain a more fundamental understanding of abiotic processes controlling abiotic reduction reactions of chromate and dichromate ions (Cr(IV)$_{aq}$). Photoemission spectroscopy (PES), photoelectron diffraction, and vacuum STM were used to characterize the composition, atomic structure, and morphology of clean surfaces of a-Fe_2O_3(0001) and Fe3O4(100) grown by molecular beam epitaxy on single crystal substrates of a-Al_2O_3(0001) and MgO(100), respectively. A simple surface autocompensation model is adequate to predict the stable termination(s) of these surfaces. In addition, interlayer relaxations were experimentally determined and found to compare favorably with predictions from molecular simulations for hematite (0001), but not for magnetite (100). Similar synthetic model surfaces, as well as clean (0001) and (1-102) surfaces of natural hematites and clean (100) and (111) surfaces of natural magnetites were reacted with controlled, sequential doses of water vapor (ranging from 10-9 to 10 torr p(H_2O) at 3 min. exposure times) under UHV conditions. These surfaces were characterized following each dose using O 1s PES. In each case, a threshold p(H_2O) of 10-4 to 10-3torr was observed, below which water vapor reacted primarily with defect sites and above which water vapor reacted with terrace sites to produce extensive surface hydroxylation. The kinetics of reduction of Cr(VI) to Cr(III) and the nature of the reacted surface layer on surfaces initially containing Fe(II) were determined by Cr and Fe L-edge and O K-edge x-ray absorption and Cr and Fe 2 p and O 1s PES on clean natural magnetite (111) samples reacted with 50µM Na2CrO4 solutions for 5 to 120 minutes. Reduction rates were found to be pH dependent, with the fastest rates occurring at pH values below the point of zero charge of magnetite (6.6). At the highest rate, the surface redox reaction is ~95% complete within 10 minutes. The reacted magnetite surfaces were found to consist of a thin (15±5 Å) layer of poorly crystalline Cr(III)-(oxy)hydroxide that passivates the surface and prevents further reduction of Cr(VI)$_{aq}$. Iron in the surface region of the magnetite substrates was simultaneously oxidized to Fe(III). The reaction rates and products are similar to those previously observed for the reaction of Cr(VI)$_{aq}$ with "zero-valent" iron. Grazing-incidence XAFS spectroscopy on Cr(III)$_{aq}$- and Cr(VI)$_{aq}$-reacted hematite (0001) and reduced hematite (0001) surfaces under ambient conditions showed that the reduction products, Cr(III)-(oxy)hydroxide surface complexes, are bound dominantly as inner-sphere edge-sharing, tridentate complexes on the oxidized surface. Competitive effects of the common aqueous oxoanions HPO_4^{2-} and SO_4^{2-} on Cr(VI)$_{aq}$ sorption on iron oxides were examined by measuring the extent of uptake and uptake kinetics of Cr(VI)$_{aq}$ reacting with hematite powder in the presence of these other oxoanions using laser photoacoustic spectroscopy and batch uptake experiments. Sorption of Cr(VI)$_{aq}$ and HPO_4^{2-} occurs even at low pH where monovalent anions predominate in solution. As a consequence, the fraction of total species in solution available in the form of divalent anions is a more important determinant of the relative amount of Cr(VI)$_{aq}$ or phosphate sorbed than the intrinsic selectivity of the anions for the surface. In mixed-anion systems typical of groundwater, significantly different sorption affinities may be observed than predicted solely on the basis of relative single-anion sorption constants.